

OFFICE OF NAVAL RESEARCH

**Grant #N00014-91-J-1630
R&T Code 313s002 --- 05**

Technical Report #19

AD-A285 565

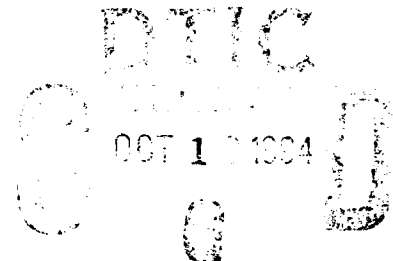


An Atomic View of Motion on Surfaces

by

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Prepared for publication in

Analytica Chimica Acta

DTIC 313s002 163005 16802

10 October 1994

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94-32544



REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE

10 October 1994

3. REPORT TYPE AND DATES COVERED

Technical 6/1/94-5/31/95

4. TITLE AND SUBTITLE

An Atomic View of Motion on Surfaces

5. FUNDING NUMBERS

N00014-91-J-1630

6. AUTHOR(S)

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K. R. Krom, S. J. Stranick, and M. G. Yoshikawa Youngquist

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Department of Chemistry
152 Davey Laboratory
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University Park, PA 16802

8. PERFORMING ORGANIZATION
REPORT NUMBER

Report #19

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
Chemistry Program
800 N. Quincy Street
Alexandria, VA 22217-5000

10. SPONSORING / MONITORING
AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Prepared for publication in *Analytica Chimica Acta*

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release.
Distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

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14. SUBJECT TERMS

15. NUMBER OF PAGES

23 pages

16. PRICE CODE

17. SECURITY CLASSIFICATION
OF REPORT

Unclassified

18. SECURITY CLASSIFICATION
OF THIS PAGE

Unclassified

19. SECURITY CLASSIFICATION
OF ABSTRACT

Unclassified

20. LIMITATION OF ABSTRACT

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Abstract

We use the scanning tunneling microscope to obtain an atomic scale view of the motion of adsorbates on surfaces. For sufficiently slow diffusion, we follow this motion in real time. For faster adsorbate motion we are able to observe the partial and transient occupancy of surface sites on the time scale of our measurements. For lateral motion induced by surface processes such as adsorption or chemical reaction, we are able to analyze the final positions of the adsorbates or reaction products in order to measure the distances covered and to elucidate the means by which energy is accommodated to the surface.

By _____	
D. I. B. No. _____	
Availability Codes	
Dist	Avail and/or Special
A-1	

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1. Introduction

Motion on surfaces is critical in chemical reactivity, film growth, corrosion, surface processing, micro/nanolithography, patterned surface stability, and many other areas [1–6]. The rates of adsorbate motion are often dominated by the effects of sites such as steps, other defects, and coadsorbates [2–9]. We study the elementary processes of surface dynamics on the atomic scale using scanning tunneling microscopy. In this way we can isolate and study the effects of these special sites on the surface dynamics.

Imaging with the scanning tunneling microscope (STM) is rather slow since the probe tip must be scanned mechanically to generate a full image of an area of the surface [10]. We take three approaches to studying the site-specific kinetics of adsorbate motion and to bring the dynamic range of our measurements into coincidence with the dynamic range of the rates studied. First, in studying the initial motion of adsorbates after sticking to the surface, we work at low surface temperature and use surface features such as steps as guideposts on the surface to act as boundaries for regions (*i.e.* atomically flat terraces) sampled by the incoming atoms or molecules [7,8]. By allowing a narrow range of incident angles, we are able to do a *post mortem* analysis of how far the incoming atoms and molecules moved across the surface. Second, we slow down the rates of motion to be comparable to or slower than our image acquisition rate by reducing the temperature at which the measurements are made [11,12]. Similarly, we can increase the attractions between adsorbates and between the adsorbates and the substrate sufficiently that the motion can be adequately followed at room temperature or even in measurements at elevated temperatures [6]. Third, we analyze the frequency composition of the tunneling current to measure molecular motions at rates as high as the microwave frequency range (this requires specially equipped STMs) [11,13,14]. Each of these methods enables us to match the time scales of our measurements to the rates of motion of adsorbates.

Following atomic motion on surfaces dates back to the first atomic resolution imaging technique — field ion microscopy (FIM) [15,16]. Soon after its invention, Binnig and co-workers applied the

STM to study the surface dynamics of the transient population of surface sites by mobile adatoms [10]. Since then, STM data has been used to analyze the kinetics of motion of adsorbates and of features such as surface steps and vacancies [10,17–21] using many of the same techniques earlier developed for FIM [15,16]. For STM measurements of mobile adsorbates at *high* surface coverage, correlation techniques have been used to analyze images in order to determine favored adsorption sites, surface ordering, and interaction energies [20,21].

2. The Roles of Special Surface Sites

Atomic resolution imaging techniques have verified the long-held belief in the field of surface science that sites such as step edges and other defects exhibit special properties with regard to binding and motion for a wide range of adsorbates [3]. For example, we have used STM measurements to show that for Xe on Pt{111} at 4K the first Xe atoms adsorbed on the surface had sufficient lateral transient mobility (discussed below) to reach step edges where they lost their momentum and stuck [7]. Thus, the initial atoms were found adsorbed at step edges. When these step edge sites were filled, Xe atoms formed clusters at point defects in the substrate surface [7,22]. This was shown by using the STM tip to slide the Xe clusters away from their initial positions, thus revealing defects in the underlying substrate [7,22]. For adsorption of a number of refractory metal atoms on Ir{111}, Wang and Ehrlich have used FIM to show that the atoms stick at point of impact [23]. This topic remains controversial [24,25] and is plagued by the paucity of experimental measurements of transient mobility [7,23,24]. A related topic is that of ballistic diffusion length: once an adsorbed atom or molecule thermally surmounts the barrier to diffusion, how far does it go before accommodating to the surface and coming to rest? While the energy loss mechanisms might well be the same in bringing adsorbates to rest, the initial distributions of adsorbate energies would typically be quite different for thermal activation vs. gas atoms or molecules that become trapped by their attraction to the surface [8,26,27]. For substitutional Pb atoms on a Ge{111} surface, Golovchenko and co-workers have observed these “long jumps” (*i.e.* of more than one lattice spacing) [28,29]. In the case of Pb on Ge{111}, the mechanism by which this motion takes place has

been assigned to highly mobile point defects resulting in the concerted motion of many atoms in single events [29].

The importance of the subject of transient mobility once again comes back to the role of special sites in surface chemistry and dynamics. If adsorbates need to reach special low density surface sites at which their reactivity is enhanced or at which growth takes place, any means by which they can reach these sites is important. Further, if heterogeneous surface or thin film structures can be grown at temperatures lower than those at which substantial diffusion takes place, then such structures would remain stable and sharp interfaces could be maintained during growth as compared to higher temperatures where components would intermix via diffusion. Such a scheme would require the adsorbates to have sufficient mobility to reach the growth edge or to utilize other properties such as preferential sticking at the growth edge.

Two examples of film growth initiating at substrate step edges are benzene and C_{60} on Cu{111} [9,30,31]. At temperatures where the molecules are mobile on the terraces, film growth starts at the substrate step edges [9,30,31]. When the motion of the benzene molecules is quenched by reducing the temperature to 4K, the molecules on the substrate terraces freeze into adsorption sites at substrate defects [9,32]. Once again, these sites are identified by sweeping the molecules away from their adsorption sites and examining the surface underneath [32].

3. Diffusion and Other Thermally Activated Surface Motion

At room temperature, diffusion of isolated adsorbates on surfaces is usually too rapid to allow imaging these adsorbates with the STM [33,34]. Thus, STM studies of adsorbate structure have concentrated on ordered overlayers in which adsorbates are locked into place by their neighbors [34]. Reducing the diffusion rate of adsorbate atoms and small molecules by reducing the system temperature is perhaps conceptually the simplest method of making diffusion improbable enough so as to be able to observe single adsorbate hops. Such experiments present quite an experimental challenge as evidenced by the few such measurements in the literature. One great step forward in this

regard was taken by Wolkow who settled a long-standing controversy regarding the orientation of Si dimers on the reconstructed Si{100} surface [35]. By reducing the temperature sufficiently, he was able to show that dimers on this surface froze into a tilted configuration [35]. Previous room temperature studies of Si{100} had observed symmetric dimers only because the motion between the two favored tilted configurations was so rapid that topographic STM measurements observed a temporal average of the two. This serves as a warning for further STM measurements of motion. If motion is extremely rapid, the STM will observe only average values of surface topography. Such a case has also apparently been observed for the rotation of azulene adsorbed on Pt{111} by Hallmark and Chiang [36]. They used the rotationally averaged topography to differentiate azulene from simultaneously adsorbed naphthalene molecules which remained predominantly in a fixed orientation [36]. As discussed below, with a substantially enhanced instrumental frequency response, it may be possible to observe electronic effects associated with rapid rotational motions directly in the tunneling current [14].

One alternative to lowering the temperature to the regime where individual hops are observable is to expand the dynamic range of measurement by reducing the scanning motion of the tip and thus measuring the presence or absence of adsorbates at a single site or at a small number of sites. This was first done by Binnig and co-workers who noted the presence or absence of O adatoms on a Ni{110} surface by monitoring the tunneling current [10]. The rapidly moving O atoms produced a current spike (dip) as they moved under (away from) the STM tip. Using conventional STM electronics, this method allows us to measure the transient occupation at hopping rates up to perhaps $10^6/\text{sec}$ [9,10]. Using this type of measurement, we have measured the occupation at interface sites between a 2D molecular solid and a coexisting 2D molecular gas [9]. These measurements were made for benzene molecules adsorbed at a small fraction of a monolayer coverage on Cu{111} [9]. Benzene molecules are bound strongly at substrate step edges and are immobilized there at 77K. On straight substrate step edges, the benzene forms an ordered 2D solid. On meandering substrate step edges, the benzene forms disordered structures, but is nonetheless held immobile. On the Cu{111}

terraces, the benzene molecules remain mobile at 77K and form a 2D molecular gas. Thus a dynamic equilibrium is set up between the 2D gas and the 2D solid. We are able to observe adsorption and desorption of the 2D gas from the (1D) edge of the 2D solid as well as diffusion of adsorbed molecules between well defined adsorption sites along the interface. An example is shown in Fig. 1. The molecules forming the 2D solid appear as two rows of features in the image labelled as 1 and 2. Adsorption sites in rows 3 and 4 are only transiently occupied. Thus the molecules in these sites appear “hashed” — the molecules move in and out of the interface sites on the time scale of imaging. The residence time of the molecules in these sites can be measured directly from the tunneling current as in ref. [10], or from the number of consecutive pixels in the images [9]. The residence times also serve as a guide as to whether the STM tip is perturbing the molecules. We find that for mild tunneling conditions ($0.1\text{V} \leq V_{\text{bias}} \leq 0.5\text{V}$ for $I_{\text{tunnel}}=100\text{ pA}$ at 77K) the residence times are independent of scan rate, resolution, and direction.

By noting that the residence times of benzene molecules at interface sites are on the order of 10 msec, but that molecules added to the step edge using the STM tip remain there for time scales >1 hour, we have shown that diffusion along the interface is more rapid than desorption from the solid edge back into the 3D gas phase [9]. This is just as for the case of adsorbate desorption from and diffusion along the surface a 3D solid. Because to a simple approximation diffusion involves breaking only a fraction of the bonds between adsorbate and (2D or 3D) solid, whereas desorption results from breaking these bonds completely, we expect the barrier to diffusion to be lower than the barrier to desorption. In the case of 3D solid surfaces, a “corrugation ratio” has been used to quantify the ratio of the barrier to diffusion vs. the barrier to desorption, and is typically 0.1–0.7 [1,37]. We are able to examine specific sites individually using the STM. In so doing we have shown that at special sites such as kinks in the substrate step edges, where the benzene molecules are more weakly bound, diffusion can be reduced and desorption enhanced to the point where adsorption/desorption is the predominant motion [9]. The ability to examine the local chemistry at specific surface sites is one of

the great strengths of using the STM to study the dynamics of special surface sites independently, and thus with exquisite specificity.

Another alternative to cooling is to reduce the rate of diffusion of surface species *chemically*. This can be done by increasing the barriers to diffusion by increasing the substrate–adsorbate and/or adsorbate–adsorbate interactions. This generally leads to complex motions such as in our measurements of diffusion within self-assembled monolayers (SAMs) of alkanethiols on Au{111} [6,38,39]. We have observed two types of motion in these films. The slower of these is shown in the two frames of Fig. 3. These show a mixed composition SAM of 25% $\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_{15}\text{SH}$ and 75% $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ on Au{111} [38]. In the 37 minutes between two sequential images, molecules within the densely packed layers have exchanged leading to coalescence of the domains of the minority surface species. The mechanism by which this motion is accomplished remains unknown. A faster motion on this surface takes place at step edges. There complexes of the alkanethiolate with the Au substrate atoms diffuse along the step edges [6]. This occurs because the S–Au interaction weakens the underlying the Au–Au bonds. The same step flow is observed for the SAM-covered Au{111} surface as for the bare Au{111} surface [4,5], but the attractive alkanethiolate–alkanethiolate interactions tether and dramatically slow the attached Au atoms [6].

Using the microwave frequency electronics of a tunable AC scanning tunneling microscope (ACSTM), it may be possible to observe periodic motion at frequencies as high as 10^{10} Hz [11,13,14]. Since molecules such as benzene perturb the electronic structure of the substrate anisotropically [14,33], motions such as free or frustrated rotations will perturb the electronic structure and thus affect the tunneling current at the frequency of motion. The electrons (more precisely, the local density of states — LDOS) distributed anisotropically about the adsorbate easily follow the motion of the molecules at these frequencies. There is nuclear magnetic resonance evidence that benzene goes from a frustrated to a free rotor as a function of temperature on Pt{111} [40,41]. Thus for free rotation of benzene in a three-fold hollow site on Pt{111}, for example, where the LDOS perturbation is nominally three-fold symmetric about the molecule [33], we would expect

to observe the tunneling current modulated at three times the rotation frequency of the molecule [14]. If the molecule were a frustrated rotor, the observed oscillations in the tunneling current would predominantly appear at this torsion frequency (at or near the extrema of the LDOS perturbation) or at twice the torsion frequency (at or near the center of the center of the LDOS perturbation, because each oscillation crosses the extrema two times). Note that this should allow us to measure even zero point motions of the molecules. McClelland and co-workers have combined field emission microscopy and streak camera techniques to observe the motion of single adsorbates in real time at frequencies up to 2×10^{12} Hz [42,43]. While we are restricted to lower frequency motions (up to $\sim 2 \times 10^{10}$ Hz), the ACSTM technique should be applicable to a broader class of surface-adsorbate combinations. Experiments to carry out the ACSTM measurements of the rotational spectra of single adsorbates are in progress.

An important issue to be addressed in studies of surface diffusion is the distribution of distances moved in elementary motions — the “ballistic diffusion length” — that is, the distance traversed in a single motion before enough energy is lost to the lattice for the adsorbate to come to rest or to scatter in a different direction. Doren and co-workers have addressed this issue of long jumps theoretically [26,27]. Experimentally, Golovchenko and co-workers have observed long jumps for the motion of substitutional Pb on Ge{111} surfaces [28,29] which they attributed to highly mobile surface vacancies and thus the concerted mechanism of many surface atoms. The surface-adsorbate potential may also be conducive to driving adsorbates to special surface sites such as steps. This is the situation found in FIM studies for Ir on Ir{111} tips by Wang and Ehrlich in which atoms which come within three lattice sites of the step riser are rapidly incorporated into the step edge [44]. By operating at low enough temperature, individual jumps and thus the ballistic jump lengths for each can be measured. Two situations where high initial energies parallel to the surface may enhance the possibility of ballistic transit of the surface are in adsorption from the gas phase [8], and in exothermic surface reaction [45]. These are discussed in the following section.

4. Transient Mobility and Two-Dimensional Scattering

One of the least studied forms of surface motion is transient mobility. By controlling the incident angle for adsorbates as in molecular beam experiments, by keeping the substrate temperature low enough so that thermally activated surface diffusion is negligible, and then by analyzing the distributions of adsorbates on the surface, we are able to determine how far on average the adsorbates move across the surface before coming to rest — the mean accommodation length [8]. We depend upon step edges to be both traps of adsorbates and to be the “earliest” point of impact in the laboratory frame. That is, the atoms with the longest distance to travel to get to the next step edge riser are those that impinge just above the riser of the previous step edge. The incident energy is determined from the thermal and geometric configuration of the instrument and crystal. For Xe on Pt{111} [7], and in our current instruments [46], the adsorbing gas impinges with a thermal energy distribution (characterized by a temperature between room temperature and its freezing point) at a well defined angle on a crystal maintained at low temperature. By properly orienting the steps on the crystal surface in the laboratory frame, the atoms transit the surface in the direction of the step edge riser. This situation is shown schematically in Fig. 4. The energy and internal state distributions of the incident particles could be further narrowed using molecular beam techniques [47]. The form of the distribution of final positions of the incident particles on the surface gives an indication as to how energy is lost to the surface in the accommodation process [8]. The excess density at the substrate step edges provides a measure of the mean accommodation length on terraces [8].

In our experiments for Xe impinging on a Pt{111} crystal held at 4K, the Xe atoms were randomly adsorbed on the terraces, and thus needed on average to travel at least half the terrace width to reach the nearest step edge in the direction of their incident component of momentum parallel to the surface [7]. Since nearly all the Xe atoms in the dilute limit were found at step edges, the accommodation length is likely to be even longer than the $\sim 600\text{\AA}$ width of the widest terraces found. Such long accommodation lengths had earlier been predicted for rare gas adsorbates by Tully and co-workers [48–50].

In another series of experiments, we set out to measure the transient mobility of benzene on Ni{110} at 77K. The higher corrugation of this more open metal surface is expected to lead to larger diffusion barriers than those found for Cu{111}. Diffusion is expected to be substantially slower on terraces of Ni{110} than on Cu{111}, but we have not measured this rate. The incident polar angle (*i.e.* the crystal surface tilt from horizontal) was set at 45° off normal. In order to increase the effective terrace width available for the incident molecules to transit, we adjusted the azimuth of the crystal such that the sagittal plane of the incident molecules also was angled with respect to the substrate step edges. This situation is shown schematically in Fig. 5. The upper terrace in Fig. 5 shows a “perfect” atomically flat terrace. The lower terrace shows the typical situation in which a small amount of H contamination leads to line defects which run perpendicular to the step edges [51,52]. The results of such an experiment are shown in Fig. 6. The arrow indicates the projection in the surface plane of the direction of incoming molecules. These features were not present immediately before dosing this Ni{110} sample. In this case, the line defects take the place of the step edges and capture essentially all the incident benzene molecules (just as substrate steps sink energy and atoms). Thus we have shown that these molecules have substantial transient mobility [46].

For Xe on Pt{111} at 4K, once the step sites were filled, as the coverage was increased the Xe atoms formed islands at point defects on the surface [7]. One question that remained was the extent to which the Xe atoms underwent 2D scattering on the surface [53,54] before coming to rest at the island edge. Surely the first incident atoms after the step sites were filled also reached the step edges. What happened to them at this point? The comb structures such as those found in Figs. 5 and 6 can be used to study 2D scattering. Only those molecules which scatter can reach the side of the line defects that are shaded from the incident adsorbates. By examining the back sides of line defects that are more or less exposed by adjacent line defects, the extent of this scattering can be determined.

5. Conclusions and Outlook

Through the use of atomic scale imaging we are able to follow the dynamics of surface motion on the atomic scale and to differentiate the site specific rates of motion. Using low temperature STMs, we

are able to reduce the rates of motion to those comparable to our imaging or to our data acquisition rates. For relatively slow motions, we observe the changes that have taken place in the area of the surface imaged. For faster rates of motion, we follow the transient occupation of single sites at the position of the probe tip.

We measure the transient mobility of atoms and molecules adsorbing onto surfaces from the gas phase by studying the distributions of these atoms and molecules, once they come to rest, in order to determine aspects of the accommodation process. These methods also apply to exothermic surface chemical reactions in which products have energy in translational degrees of freedom.

Finally, we have followed the motion of complex systems such as self-assembled monolayers of alkanethiols on Au{111} in order to see the effects that this motion has on the nanometer scale structures and stability of these films. We have discovered a novel diffusion mechanism in which the adsorbates move complexed to substrate atoms and an exchange mechanism which leads to the reorganization of nanometer scale surface structures. In all these measurements we are able to isolate the critical roles played by special surface sites such as steps and other defects.

6. Biographical Note

Paul S. Weiss is an Assistant Professor of Chemistry at The Pennsylvania State University, 152 Davey Laboratory, University Park, PA 16802, USA. He studied at the Massachusetts Institute of Technology and the University of California at Berkeley. He held post-doctoral positions at AT&T Bell Laboratories, Murray Hill and at the IBM Almaden Research Center. He investigates the chemistry and physics of surfaces using scanning tunneling microscopy/spectroscopy and other techniques.

Acknowledgments

The authors would like to thank Dave Allara, Tim Dunbar, and Atul Parikh for preparation of self-assembled monolayer films, and Mark Cardillo, Doug Doren, Ted Einstein, Eric Garfunkel, Barbara Garrison, and Joe Meyer in addition to the above for helpful discussions. This work was supported by the National Science Foundation, the Office of Naval Research, the Petroleum Research Fund administered by the American Chemical Society, AT&T Bell Laboratories, the Biotechnology Research and Development Corporation, Eastman Kodak, Hewlett-Packard, and IBM.

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Figure Captions

1. A scanning tunneling microscope image recorded at 77K of a $22\text{\AA} \times 22\text{\AA}$ area of a $\text{Cu}\{111\}$ surface covered by a fraction of a monolayer of benzene. The benzene molecules are mobile on the atomically flat terraces but are held rigidly at step edges. The image was recorded in UHV using constant current mode with $V_{\text{tip}} = -0.100\text{ V}$ and $I = 100\text{ pA}$ and is shown unfiltered. Topography is displayed. Row 1 is just below the step riser. Row 2 is just above the step riser.
2. A scanning tunneling microscope image recorded at 4K of a $350\text{\AA} \times 280\text{\AA}$ area of a $\text{Cu}\{111\}$ surface covered by a fraction of a monolayer of benzene. The translational motion of the benzene molecules is frozen out everywhere on the surface. The image was recorded in UHV using constant current mode with $V_{\text{tip}} = -0.100\text{ V}$ and $I = 100\text{ pA}$ and is shown unfiltered. Derivative along the fast scan direction (horizontal in the image) is displayed so that the surface appears as if illuminated from the left.
3. A sequential pair of scanning tunneling microscope images recorded at room temperature in air of a $500\text{\AA} \times 350\text{\AA}$ area of a mixed composition self-assembled monolayer of 25% $\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_{15}\text{SH}$ and 75% $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ on $\text{Au}\{111\}$. The $\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_{15}\text{SH}$ domains appear brighter in the images. Images a) and b) were recorded 37 minutes apart using constant current mode with $V_{\text{tip}} = -0.100\text{ V}$ and $I = 100\text{ pA}$ and are shown unfiltered. The arrows indicate motion of the domain boundaries leading to coalescence of two domains.
4. A schematic illustrating how a goniometer orients a crystal surface in the laboratory frame in the low temperature microscope. Steps on the crystal surface generally run in one direction due to slight crystal miscuts. The incoming atoms or molecules come line-of-sight from the room temperature UHV chamber as in a collimated molecular beam. The steps on the surface run uphill as viewed by the incoming atoms or molecules. If the incoming particles have very long accommodation lengths on terraces, they reach and stick to the step riser that bounds the terrace on which they impact.

5. A schematic illustrating the incident angle of benzene molecules on the Ni{110} surface. The upper terrace is shown without line defects. The lower terrace is shown with line defects. Benzene molecules are shown as disks crossing the surface. Notice how the line defects catch the molecules before they reach the step edge. This is the situation we found experimentally when H contamination caused line defects on the surface, as shown in Fig. 6.
6. A scanning tunneling microscope image recorded at 82K of a $250\text{\AA} \times 160\text{\AA}$ area of a Ni{110} surface covered by a small fraction of a monolayer of benzene. The benzene molecules transit the surface upon impact until they run into line defects (see text) where they bind preferentially and are rigidly held. This situation is shown in the lower terrace in the schematic of Fig. 5. The STM image was recorded in UHV using constant current mode with $V_{\text{tip}} = -0.100\text{ V}$ and $I = 100\text{ pA}$ and is shown unfiltered. Derivative along the fast scan direction (horizontal in the image) is displayed so that the surface appears as if illuminated from the left. The arrow indicates the projection in the surface plane of the direction of the incident molecules.

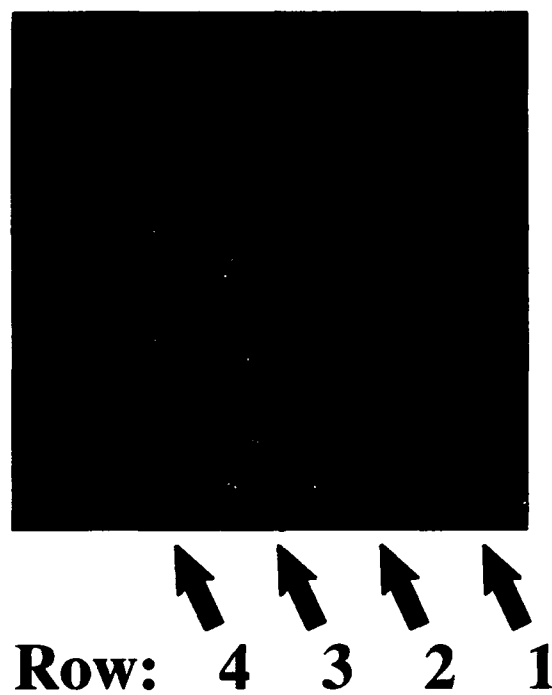


Fig. 1



Fig. 2

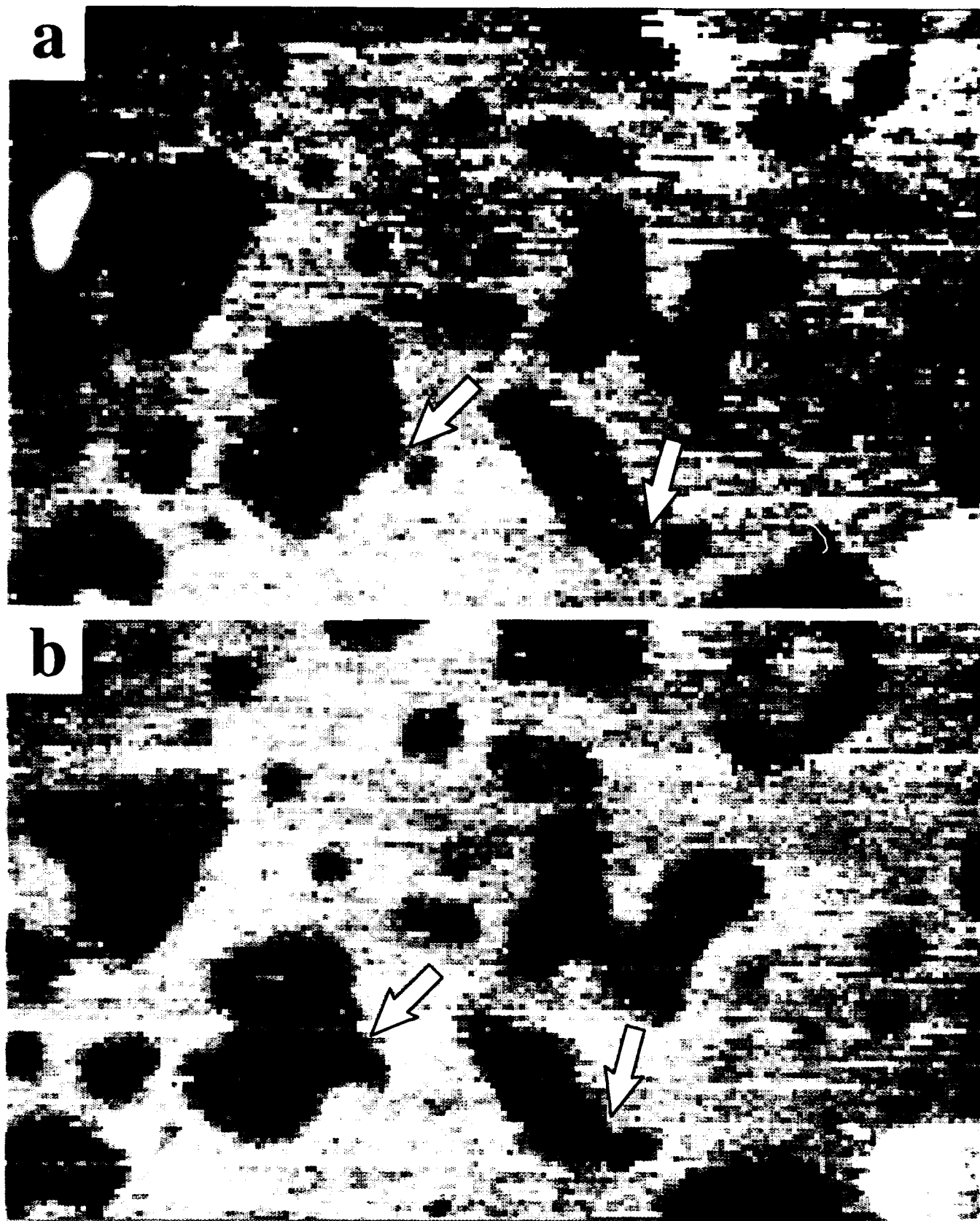


Fig. 3

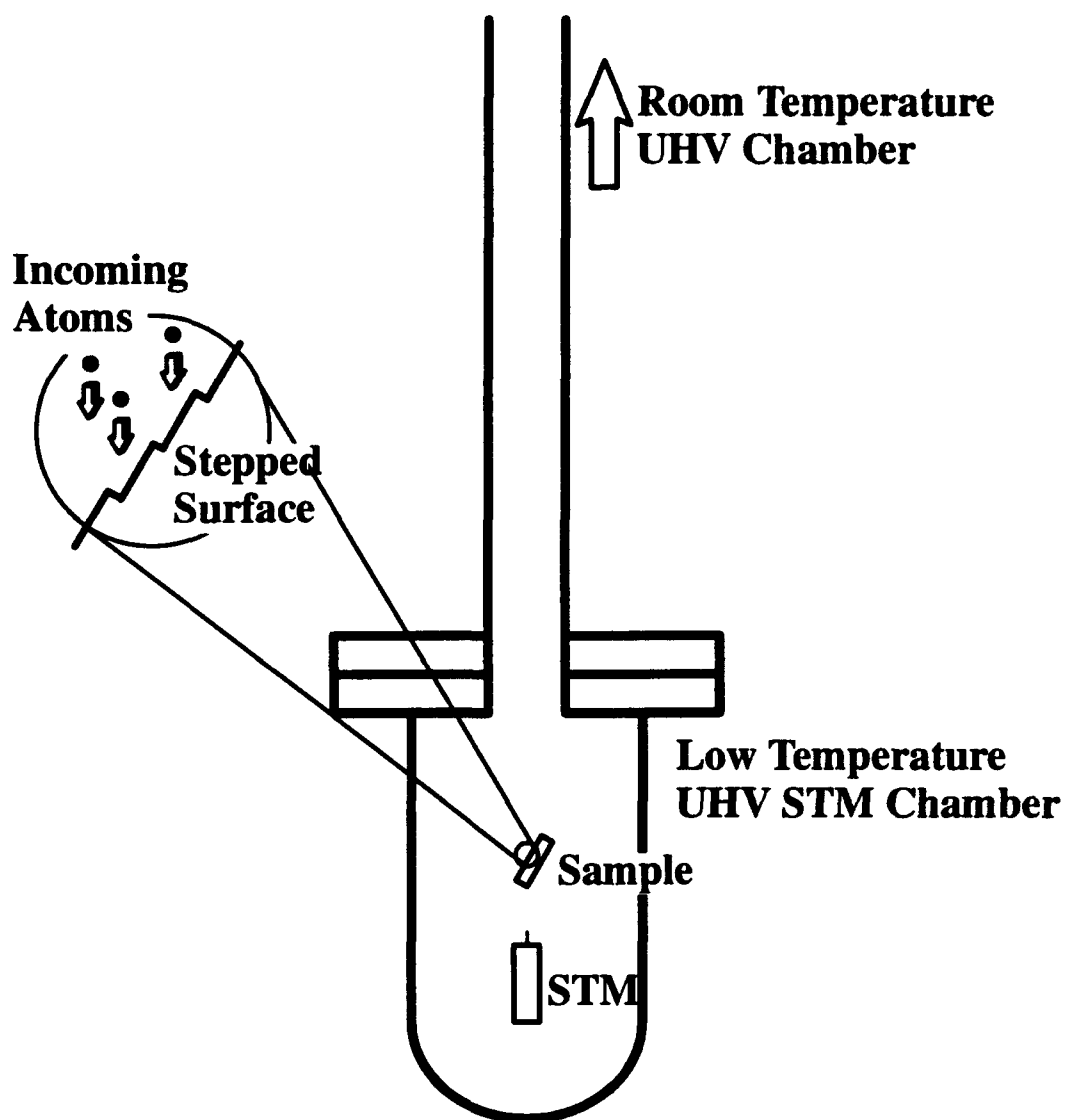


Fig. 4

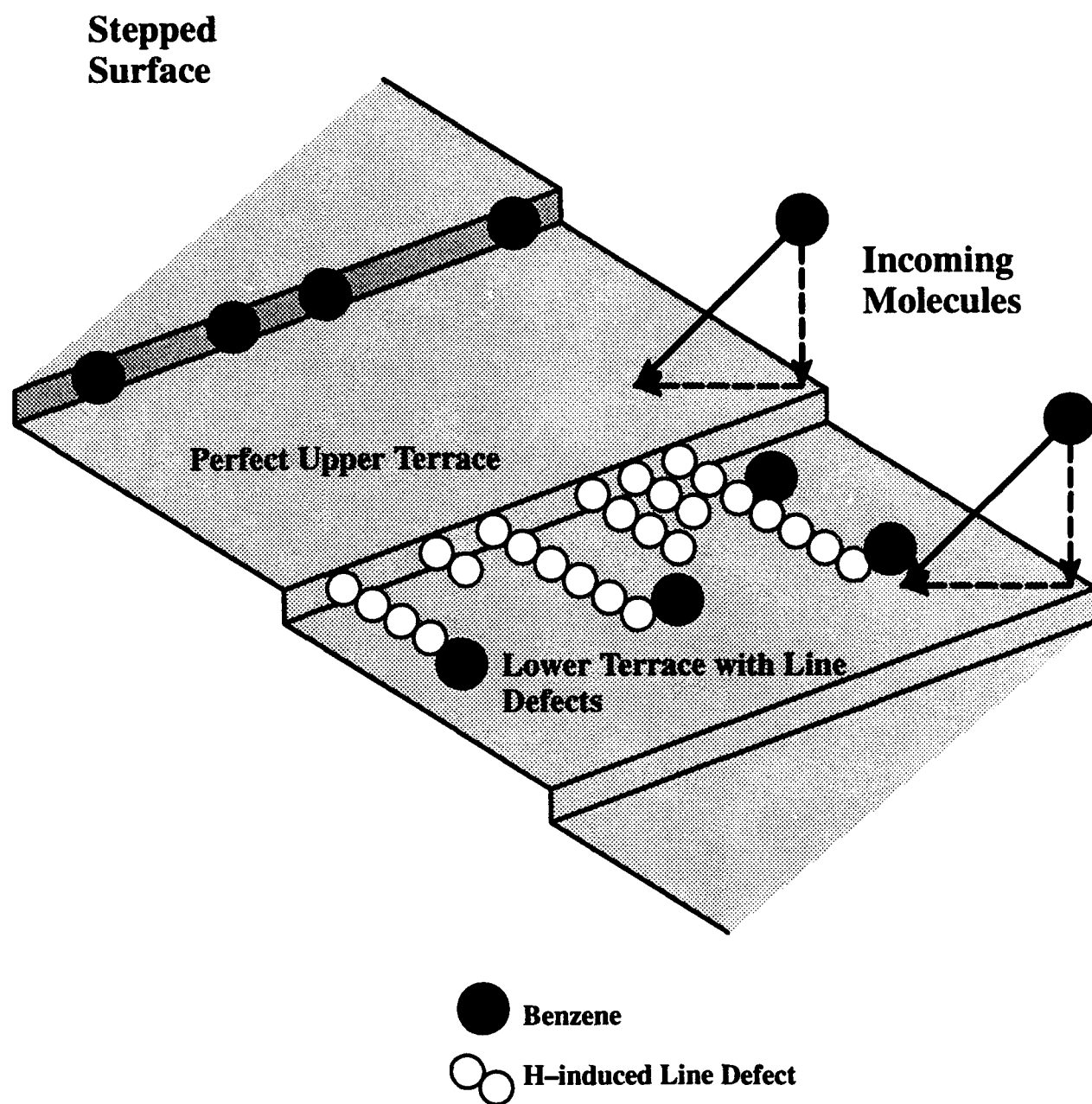


Fig. 5

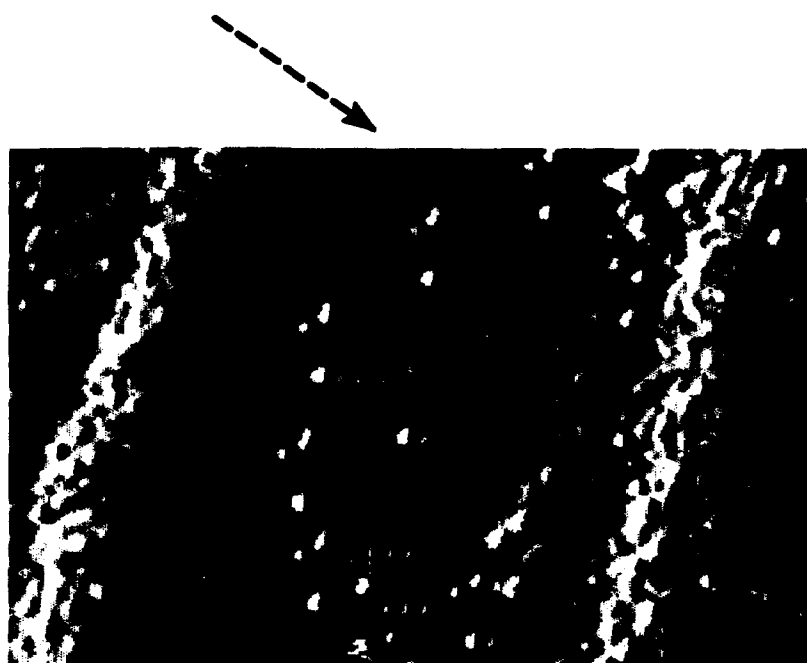


Fig. 6